

Luminescence Properties of Semiconductor Nanoparticles

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ABSTRACT

Luminescence studies in nanostructures is a current topic of research. In low dimensional systems electron and holes are spatially confined causing quantum confinement effects. It has been found that the efficiency and Stokes shift of low dimensional system increases with decreasing size R of the semiconductor nanoparticles. It has been found that the size-dependence of the luminescence efficiency η and makes a comparison between the theoretical experimental values of η .

Keywords: Semiconductor nanoparticles, Luminescence and optical properties.

INTRODUCTION

In the recent past, nanomaterials have drawn greater attention of scientific community due to their size specific properties that are different from the bulk materials.

Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, thermal, etc.) due to surface effects and quantum size effects. Owing to the extremely small dimensions, these materials exhibit properties, which are fundamentally different from, and often superior to those of their conventional counterpart. In recent past, there has been considerable interest in the study of size

effect in semiconductors of reduced dimension (in nanometer scale) due to their applications in optoelectronic devices, single electron devices, resonant tunneling devices, memory devices, magnetic sensors, catalysis, etc.¹⁻⁵ Optical spectroscopy being the non-contact method, has proved to be the most suitable technique to monitor the size-evolution of the electronic structure. The present studies we have investigated the energy conversion and Stokes shift properties of semiconductor nanoparticles.

THEORY

(I) ENERGY CONVERSION CHARACTERISTIC

In bulk crystalline ZnS:Mn, the partially spin-forbidden $Mn^{2+} {}^4T_1 \rightarrow {}^6A_1$ transition has a lifetime of 1.8 ms at room temperature. In ZnS:Mn of 3nm size there are two lifetimes $\tau_1=3.7ns, \tau_2=20.5ns$. In ZnS : Cu $\lambda_{em}=480nm, \tau_1=2.9ns, \tau_2=20.5ns$, two different recombination centers may be involved in nanoparticles firstly the recombination centers lying on surface and secondly the recombination centers lying inside the bulk.

To interpret these observation it is suggested that the hybridization of s-p electron state of host with the d-electron state of Mn^{2+} , is caused to a significant extent by the spatial overlap of these states owing to the confinement.

The luminescence efficiency η may be expressed as:

$$\eta = \frac{\alpha_r}{\alpha_r + \alpha_{nr}} \quad (1)$$

α_r and α_{nr} are radiative and non-radiative rates, respectively.

The radiative recombination takes place at the surface. Thus, α_{nr} should depend on the number of surface atoms per units volume and it may be expressed as:

$$\alpha_{nr} \propto \frac{4\pi R^2}{\frac{4}{3}\pi R^3} \propto \frac{1}{R} \quad (2)$$

α_r should depend on the number of Mn^{2+} at Zn^{2+} sites. In case of a single Mn^{2+} ion within a nanocrystal may expressed as:

$$\alpha_r \propto R^{-3} \quad (3)$$

Thus from Eqs (1), (2) & (3) we get:

$$\eta = \frac{\frac{C_1}{R^3}}{\frac{C_1}{R^3} + \frac{C_2}{R}} = \frac{1}{(1 + \beta R^2)} \quad (4)$$

$$\text{where } \beta = \frac{C_2}{C_1}$$

(II) STOKES SHIFT CHARACTERISTIC

Fig 1) shows that the Stokes shift of ZnTe nanocrystals increases with reducing size of nanocrystals⁶. Similer effect has been observed for ZnS:Mn and CdS nanocrystals.

It is known that the number of phonons emitted just after the absorption transition in the configuration coordinates of $q = 0$ is given by:

$$S = \frac{M_a \Omega q_o^2}{2h} \quad (5)$$

where M_a = mass of the atom, Ω = vibrational frequency, q_o = the configuration coordinate corresponding to the minimum energy of the excited state and h = Planck's constant.

The increase of Stokes shift with reducing size of the nanocrystals Is not satisfactorily understood to date. It seems that increasing value of both Ω and q_o may be responsible for this fact.

EXPERIMENTAL SUPPORT TO THE PROPOSED THEORY

Fig. 2) shows the size dependence of the luminescence efficiency of ZnS:Mn

nanoparticles. It is seen that the dependence of η or R of Eq (4). To perform this experimental⁴ precipitated, nanocrystalline ZnS powder by reacting diethylzinc with hydrogen sulfide in toluene to form ZnS. Bulk ZnS is usually doped by thermal diffusion at high temperatures [$>1100^\circ\text{C}$] but since nanocrystallites sinter at extremely low temperatures, they must be doped during precipitation. To dope the ZnS: Manganese chloride is reacted with ethylmagnesium chloride to form diethylmanganese in a tetrahydrofuran solvent and added to the reaction. The separation of the particles is maintained by coating with the surfactant methacrylic acid. In the coated ZnS:Mn particle system a gradual but significant increase is observed in the luminescent intensity of Mn^{2+} emission when exposed to exciting 300nm UV light (UV curing) and the photoluminescent efficiency of 27-33Å ZnS:Mn nanocrystalline powder is about 18% at room temperature.

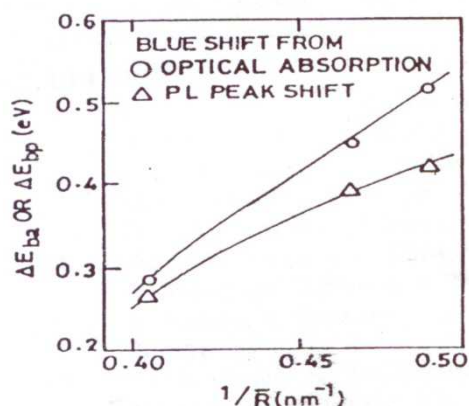


Fig.1 Dependence of the blue shifts (ΔE_{ba} and ΔE_{bb}) Obtained from the optical absorption (ΔE_{ba}) and the PL peak shift (ΔE_{bb}) on the $1/R$, where R is the average grain radius in nm.

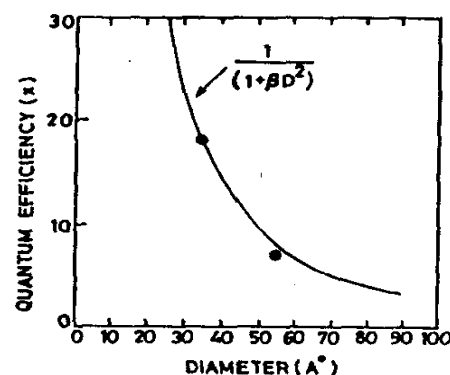


Fig.2 Variation of luminescence quantum efficiency of ZnS: Mn^{2+} nanocrystals as a function of the radius. The solid line represents the equation $1/(1+\beta R^2)$.

CONCLUSIONS

The important conclusions are drawn from the present investigation :

- (i) It is found that the stokes shift increase with the decreasing size of nanoparticles.
- (ii) It is found that the luminescence efficiency of ZnS:Mn nanocrystals increases with decreasing size R and follows the relation:

$$\eta = \frac{1}{(1 + \beta R^2)}$$

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